

English translation of excerpts of
Japanese Patent KOKAI 2001-293335

Title of the Invention:

Method for treating waste gas containing fluorine-
containing compounds

Claims

Claim 1. A method for treating a waste gas containing a fluorine-containing compound by separating solids from the waste gas containing a fluorine-containing compound and subsequently treating the resulting gas with a catalyst comprises using, as the catalyst, γ -alumina having a crystal structure which generates diffraction rays having an intensity of 100 or more appear at five diffraction angles of $33^\circ \pm 1^\circ$, $37^\circ \pm 1^\circ$, $40^\circ \pm 1^\circ$, $46^\circ \pm 1^\circ$, and $67^\circ \pm 1^\circ$ out of the diffraction angles 2θ measured by an X-ray diffractometer.

Claim 2. The method for treating a waste gas containing a fluorine-containing compound according to claim 1, wherein said γ -alumina is heated at 600 to 900°C, and furthermore at least one auxiliary decomposition gas of H_2 , O_2 , and H_2O is added.

Claim 3. The method for treating a waste gas containing a

fluorine-containing compound according to claim 1 or 2 further comprising a step of removing an acidic gas from the treated waste gas.

Claim 4. An apparatus for treating a waste gas containing a fluorine-containing compound which comprises a solid matter separation apparatus for separating solids from the waste gas containing a fluorine-containing compound and a catalyst treatment apparatus for treating the waste gas from said solid matter separation apparatus with a catalyst, said catalyst treating apparatus being packed with γ -alumina having a crystal structure which generates diffraction rays having an intensity of 100 or more at five diffraction angles of $33^\circ \pm 1^\circ$, $37^\circ \pm 1^\circ$, $40^\circ \pm 1^\circ$, $46^\circ \pm 1^\circ$, and $67^\circ \pm 1^\circ$ out of the diffraction angles 2θ measured by an X-ray diffractometer.

Claim 5. The apparatus for treating a waste gas containing a fluorine-containing compound according to claim 4 further comprising an addition means to add at least one of H_2 , O_2 , and H_2O as the auxiliary decomposition gas to the waste gas from said solid matter separation apparatus.

Claim 6. The apparatus for treating a waste gas containing a fluorine-containing compound according to claim 4 or 5 comprising a heating means to heat the γ -alumina in said catalyst treatment apparatus at 600 to 900°C.

Claim 7. The apparatus for treating a waste gas containing a fluorine-containing compound according to any one of claims 4 to 6 further comprising an acidic gas removal apparatus for removing an acidic gas from the waste gas from the catalyst treatment apparatus.

Excerpts of Specification

From page 3, column 3, line 2 to page 4, column 6, line 46
(Paragraphs [0009] to [0035])

Originally, active alumina means a hydrate (trihydrate: $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, monohydrate: $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) and an intermediate of α -alumina (dense structure) and is represented by Al_2O_3 .

Active alumina is classified into 7 types (κ -, θ -, δ -, γ -, η -, χ -, and ρ -types) of metastable aluminas, and these aluminas can be generally obtained by the heat treatment of an alumina hydrate and contain 0 to 0.5 moles of water per mole of Al_2O_3 , and the water content varies by the temperature of the heat treatment.

γ -Alumina is one of these active aluminas, and an alumina having a specific crystal structure (a pattern of an X-ray diffraction peak) is regarded to be unstable and high in activity. And, various types of γ -aluminas having different activities can be produced depending on the type of the hydrate and the difference in the production method.

With respect to the γ -aluminas having these various crystal structures, the present inventor has found as the result of the investigations on the decomposition performance of fluorine-containing compounds by the difference in the crystal structure that γ -alumina having a crystal structure which generates diffraction rays having an intensity of 100 or more at five diffraction angles of $33^\circ \pm 1^\circ$, $37^\circ \pm 1^\circ$, $40^\circ \pm 1^\circ$, $46^\circ \pm 1^\circ$, and $67^\circ \pm 1^\circ$ out of the diffraction angles 2θ measured by an X-ray diffractometer (hereinafter referred to as " γ -alumina having this crystal structure" when the term "the present γ -alumina" is mentioned) particularly has excellent decomposition performance, and has completed the present invention.

The γ -alumina having this crystal structure can be obtained, for example, by firing an alumina sol in the form of a spherical alumina hydrogel $[\text{Al}(\text{OH})_y \cdot n\text{H}_2\text{O}]$.

Further, the content of Na_2O in the present γ -alumina is preferably 0.02% by weight or less in the entire γ -alumina amount from the standpoint of the decomposition performance of fluorine-containing compounds.

The shape of the γ -alumina which can be used in the present invention is not limited if it has said crystal structure, and is preferably spherical from the standpoint

of handling. Further, the particle size of the γ -alumina which can be used in the present invention is preferably fine so as to increase the contact area within the range of raising no gas flow resistance, and it is particularly preferred that the particle size is 0.8 mm to 2.6 mm.

As the concrete example of such γ -alumina, the trade name "NEOBEAD GB-08" (a product of Mizusawa Chemical Co., Ltd.) can be mentioned.

In order to conduct the method for treating a waste gas according to the present invention, the waste gas containing a fluorine-containing compound can be subjected to the treatment with the use of the present γ -alumina having said crystal structure as the catalyst. And, the γ -alumina is heated preferably at 600 to 900°C, more preferably at 650 to 750°C.

As the fluorine-containing compound which can be treated by the present invention, a fluorinated hydrocarbon such as CHF_3 and a perfluoro-compound (PFC) such as C_2F_6 , C_3F_8 , SF_6 , and NF_3 can be mentioned.

As the waste gas containing said fluorine-containing compound, there can be mentioned a waste gas to be discharged from the step of dry cleaning the inner surfaces and the like of a semiconductor production apparatus and

the step of etching various films in the semiconductor industry can be mentioned.

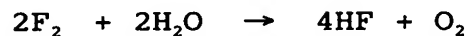
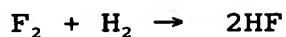
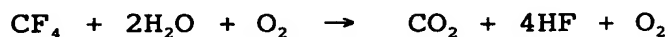
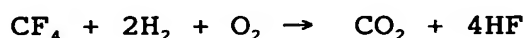
Further, in a preferred embodiment of the present invention there is provided a method which can efficiently decompose PFC and, in addition, can treat an oxidizing gas, an acidic gas, CO as well.

The waste gas to be discharged from the semiconductor production step contains not only PFC but also additionally an oxidizing gas such as F_2 , Cl_2 , and Br_2 , an acidic gas such as HF, SiF_4 , COF_2 , HCl, HBr, $SiCl_4$, and $SiBr_4$, and CO. When these gases are tried to be subjected to wet treatment, there has been a problem such that they cannot be completely disposed with water alone and require the use of an alkali agent and a reducing agent to complicate the apparatus and, in addition, to increase the cost. Further, CO is by-produced on decomposing PFC, and thus, it is necessary to decompose and remove this CO.

In a preferred embodiment of the present invention, at least one auxiliary decomposition gas of H_2 , O_2 , and H_2O is added to effect pretreatment. By using such an auxiliary decomposition gas, the life of the present γ -alumina as the catalyst can further remarkably be prolonged to efficiently conduct said waste gas treatment for a longer period of time. Also, the CO to be generated as the by-

product in the decomposition step of PFC can be efficiently decomposed.

When said auxiliary decomposition gas is added, a fluorine-containing compound such as PFC, an oxidizing gas, and CO are decomposed into an acidic gas and CO₂ in accordance with the following reaction formulae.



Namely, CF₄ is decomposed into CO₂ and HF by the reaction with H₂ and O₂ or H₂O, and an oxidizing gas such as F₂ is decomposed into an acidic gas such as HF by the reaction with H₂ or H₂O, and CO is oxidized to CO₂.

Here, as to the amount of H₂ and O₂ or H₂O to be added, with respect to PFC, the amount of H₂ and/or H₂O is preferably set at at least the molar number necessary for the F atom in the PFC to come to HF and the amount of O₂ is preferably set at at least the molar number (minimum value) necessary for the C atom to come to CO₂. Furthermore, the amount of H₂ and/or H₂O is preferably set at 6 to 20 moles per mole of PFC and the amount of O₂ is preferably set at at least said minimum value plus one mole. Further, with

respect to the oxidizing gas, the amount of H_2 is preferably set at at least the molar number necessary for the halogen atom (X) in the oxidizing gas to come to an acidic gas (HX).

As one working embodiment for conducting the treatment method according to the present invention, there can be mentioned an apparatus having a solid matter separation apparatus for separating solids in a waste gas, a catalyst treatment apparatus packed with the present γ -alumina having said crystal structure, and an acidic gas treatment apparatus which are connected to one another through piping.

Here, as the solid matter separation apparatus and the acidic gas treatment apparatus, the conventionally known ones can be used without any restriction. For example, a water scrubber (water spray tower) and the like can be used.

Further, said catalyst treatment apparatus preferably has a heating device for heating the γ -alumina relating to the present invention. As the concrete example, there can be mentioned a catalyst treatment apparatus which is composed of a cylindrical packed column and whose outer peripheral surface is covered with a heater, upper surface of said packed column is connected to an inlet for a waste gas and lower surface is connected to a discharge pipe for the waste gas after the treatment. Said packed column is filled with said γ -alumina and used.

The method for treating a waste gas relating to a preferred embodiment of the present invention can be conducted, for example, by the following manner.

First, a waste gas is introduced into the solid matter separation apparatus of the former stage where solids are separated. Further, the γ -alumina relating to the present invention filled in the packed column is heated at 600 to 900°C by said heater, and subsequently the waste gas from which solids have been removed is passed through a γ -alumina-packed catalyst treatment apparatus together with said auxiliary decomposition gas to decompose a fluorine-containing compound such as PFC into an oxidizing gas and CO_2 , and furthermore to simultaneously decompose the oxidizing gas and CO. Thus, said auxiliary decomposition gas and said waste gas are preferably introduced, as the mixed gas, into the catalyst layer formed by packing a catalyst.

Only the acidic gas (HX) and CO_2 are present in the waste gas from the catalyst treatment apparatus, and the acidic gas is removed by the acidic gas treatment apparatus such as a water spray tower, and thus the waste gas treatment can be completed.

Fig. 1 shows a schematic flow view of the waste gas treatment apparatus relating to a preferred embodiment of

the present invention. In Fig. 1, numeral 1 is a solid matter separation apparatus (a water spray tower); numeral 2 a layer packed with the γ -alumina having a specific structure relating to the present invention; numeral 3 a catalyst treatment apparatus; numeral 4 a washing water-circulation pump; numeral 5 an acidic gas treatment apparatus; numeral 6 an FT-IR analyzer; numeral 7 an air injector; and numeral 8 a bypass valve.

A waste gas 9 containing PFC, an oxidizing gas, an acidic acid, and CO is first passed through the solid matter separation apparatus of a spray tower where solids and Si compounds are removed. Then, the gas is passed through the catalyst treatment apparatus 3 packed with the present γ -alumina 2, and H_2 and O_2 and H_2O are introduced thereto to decompose the PFC, the oxidizing gas, and CO into an acidic gas and CO_2 . Furthermore, the acidic gas is removed by the acidic gas treatment apparatus 5 of the latter stage of a spray tower and discharged as the treated gas 10. Further, in order to adjust the pressure in these apparatus, it is preferred to include an air injector 7 and an FT-IR analyzer to control the treated gas in the apparatus. As the water to be used for the spray towers, water 11 is introduced into the spray tower of the acidic gas treatment apparatus 5 and the used water is supplied by

a washing water circulation pump 4 and used in the spraying for the solid matter separation apparatus 1, and then the used water is discharged as the waste water.

The present invention will now be concretely explained by examples but the present invention is not construed to be limited thereto.

Example 1

As the γ -alumina having a crystal structure which generates diffraction rays having an intensity of 100 or more at five diffraction angles of $33^\circ \pm 1^\circ$, $37^\circ \pm 1^\circ$, $40^\circ \pm 1^\circ$, $46^\circ \pm 1^\circ$, and $67^\circ \pm 1^\circ$ out of the diffraction angles 2θ , a commercially available product of Mizusawa Chemical Co., Ltd. (trade name "NEOBEAD GB-08", Na_2 content of not greater than 0.01% by weight) was used. Further, the particle size was set at 0.8 mm. The crystal structure of "NEOBEAD GB-08" was confirmed by using an X-ray diffraction analyzer RINT-2000 manufactured by Rigaku Electric Co., Ltd. with the use of $\text{CuK } \alpha$ -ray as the X-ray source. As the packed column, a quartz column having an inner diameter of 25 mm was used and packed with said γ -alumina to a layer height of 100 mm. This packed column was amounted on a ceramic tubular electric furnace and the catalyst layer was heated to 800°C .

A pseudo-waste gas obtained by diluting CF_4 with an N_2 gas was mixed with H_2 and O_2 as the auxiliary gas so as to render the atomic amount of H equal to or more than the atomic amount of F of CF_4 with respect to the amount of H_2 and to render the amount of O_2 not less than the equimolar amount of H_2 to be introduced, and the resulting mixed gas was introduced into said packed column at a flow rate of 408 sccm with inflow concentrations of CF_4 of 1% by weight, H_2 of 3.0% by weight, and O_2 of 5.7% by weight in the mixed gas. In order to observe the treating performance, the treated gas to be discharged from the outlet of the column is suitably analyzed, and when the removal ratio of CF_4 is reduced to 98% or less, the flow of the gas is stopped, and the treated amount of CF_4 was obtained from the amount of the passed gas by that time. The analysis of CF_4 was conducted by a mass detector-equipped gas chromatograph.

As the result, the removal ratio was decreased to 98% or less 920 minutes after passing the gas and the treatment amount was obtained from the passed amount of CF_4 at this point of time and was 77 L/L. The discharge concentration of CO during this time was continually an acceptable concentration (5 ppm) or less.

Fig 1

